Coupled carbonate mineral dissolution and growth: calcite and strontianite

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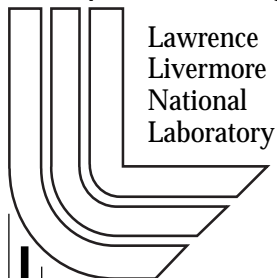*Department of Chemistry, Wright State University, Dayton, OH*

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ABSTRACT: As part of a larger project aimed at reconciling results from microscopic and macroscopic reactive transport experiments and modeling, we studied the coupled dissolution of calcite and growth of strontianite. Although our analyses are ongoing, preliminary results suggest that the experiments designed to examine the two scales yielded similar results in terms of processes. Quantification of rates extracted from experimental results at each scale continues. The comparison of macroscopic experimental results to *a priori* reactive transport simulation presented here shows that, in general, the model over-predicts both dissolution and growth rates to some extent. The model does represent processes well and captures solution concentrations in time and mineral distribution in space for the macroscopic experiment reasonably well.

1 INTRODUCTION

The ability to accurately scale-up from microscopic reactive transport processes (e.g. studied using the Hydrothermal Atomic Force Microscope – HAFM (Higgins et al. 1998)) to the corresponding macroscopic ones (e.g. studied using the Plug Flow Reactor – PFR) and having them both coincide with *a priori* geochemical modeling simulation is a holy grail of aqueous geochemistry. This work is directed towards that goal.

Because carbonate mineral dissolution and growth rates are reasonably rapid, they are amenable to study at both microscopic and macroscopic scales. Furthermore, carbonate minerals are important players in mineral-trapping of carbon in CO_2 sequestration, in metal contaminant transport in general, and in soil development. For these reasons we chose to use the carbonate minerals calcite and strontianite as vehicles for trying to scale-up our prior HAFM molecular-scale studies of coupled dissolution and growth processes (Greer et al. 2002) to the macroscale represented by corresponding PFR experiments. These PFR experiments were also amenable to simulation using reactive transport codes.

In this paper we present the preliminary results of the PFR experiment and the reactive transport simulation of coupled calcite dissolution and strontianite growth.

2 MATERIALS AND METHODS

2.1 *Solutions and minerals*

The PFR was packed with crushed, optically clear spar calcite obtained from Ward's Minerals. The grains were sieved to between 425-850 μm and cleaned repeatedly in alcohol using an ultrasonic bath. The estimated geometric specific surface area is 52 cm^2/g. The inflowing solution was prepared from reagent grade 0.002 m $Sr(NO_3)_2$ in a 0.01 m $NaNO_3$ background electrolyte made using 18 MΩ-cm deionized water, assumed to be equilibrated with the atmosphere. The measured pH was 5.5, while the pH calculated for this solution using EQ3/6 (Wolery et al. 1990) and assuming equilibration with the atmosphere is 5.6, supporting this assumption.

2.2 *Experimental and analytical apparati*

The design of the PFR is described in detail in Knauss et al. (2004). It uses a recoverable Au liner that permits easy sub-sampling of the reacted core to map out mineral distributions in space. Flow is precisely controlled using a Quizix pump and a back pressure regulator maintains system pressure. The high aspect ratio (length:diameter = 50:1) makes the PFR an ideal 1D physical model.

The aqueous solutions were analyzed for cations using ICP-ES. Solids were analyzed using AFM, SEM/EDS and XRD techniques. The solution pH was measured using a solid state ISFET pH probe, following NIST protocol.

3 EXPERIMENTAL DESIGN

We had earlier studied coupled calcite dissolution and strontianite growth at 40°C using the HAFM (Greer et al. 2002). However, preliminary reactive transport modeling suggested that the amount of strontianite produced at 40°C in our PFR using the same mass flow rate as in the HAFM would be diffi-

cult to quantify using macroscopic techniques, e.g. XRD. Simulations suggested that at 100°C easily measurable quantities of strontianite should be produced, permitting us to map out its distribution in space. Consequently, the $Sr(NO_3)_2/NaNO_3$ solution was passed through the 30 cm core, held isothermally (i.e. without a thermal gradient along its length) at 100°C for 2 weeks. A back pressure of 5 MPa was maintained to prevent atmospheric gases from exsolving upon entering the furnace, thus, a single liquid phase existed in the core during the run.

Based on the *a priori* modeling, and the chosen mass flow rate (500 g/d, equivalent to a Darcy flux of 6812 m^3/m^2-y in the PFR), we collected samples closely spaced in time over the first 2 days and then, when modeling predicted achievement of steady-state, we sampled less frequently. As a consequence, pH was not measured during the first day of the experiment. The solution pH was measured on later samples that had cooled to near room temperature and at least partially degassed, i.e. they had not re-equilibrated with the atmosphere at room temperature. Sampling for cations, however, was performed even during the core heat-up phase, which lasted 60-90 minutes.

At the conclusion of the run the gold core liner was removed and cut into 1 cm sections. The solids recovered from each section were then examined using SEM/EDS, AFM and XRD methods.

4 REACTIVE TRANSPORT MODELING DESIGN

4.1 *Thermodynamic and kinetic data*

The thermodynamic data used in model calculations were taken from the EQ3/6 database (Wolery et al. 1990). Although preliminary simulations were run with the entire suite of minerals in the database, based on their stability under these experimental conditions, only the minerals calcite and strontianite were active in the problem. The rate law used in the reactive transport model (see below) allows for parallel rate laws for each mineral, spanning the pH range. For the acid catalyzed and neutral pH rate laws we have extracted kinetic parameters from Sonderegger (1976) for strontianite and from Alkattan et al. (1998) and Chou et al. (1989) for calcite.

4.2 *Reactive transport simulator*

We used the reactive transport code CRUNCH (Steefel 2001), which coupled a chemical model with simplified fluid flow, to simulate the results of injection of the $Sr(NO_3)_2/NaNO_3$ solution through the calcite core and have accounted for mineralogical changes along the flow path. The rate law that we used in CRUNCH had a transition-state-theory-like (Laidler 1987) formulation that accounts for ki-

netic inhibition or catalysis by any species in solution. In this formulation the same rate law was used to describe both dissolution and growth according to the principle of microscopic reversibility and this is, most certainly, an empirical approximation anywhere in free energy space removed from equilibrium.

CRUNCH was used to help design the experiment, and then the results from the PFR experiment (an ideal 1D physical model) were used to evaluate the performance of the model. This direct simulator validation is a critical, but rarely taken, step in the development and acceptance of reactive transport simulators.

5 RESULTS & DISCUSSION

5.1 *PFR experimental data*

5.1.1 *Aqueous phase*

In Figure 1 we plot the aqueous concentration data and pH for samples from the PFR experiment.
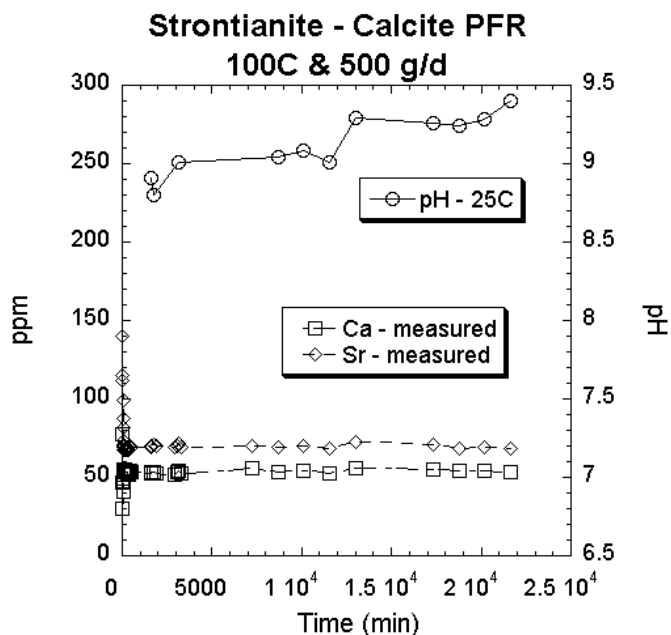

Figure 1. PFR measured concentrations and pH.

We have plotted all the data from the 2-week experiment, although it is clear that a steady-state was achieved early in the run, as predicted (see below). In Section 5.2 we will replot the measurements for the first few hours of the experiment in order to compare them more clearly to the simulated results.

5.1.2 *Solid phase*

The SEM examination of the reacted grains showed that at the front of the core, the solution was clearly undersaturated with respect to calcite evidenced by the presence of etch pits. It also showed that a secondary mineral was growing in abundance on the surface, coating the calcite grains and in places loosely cementing them to each other. Where the

coating was pulled away from the underlying calcite grain, the coupled nature of the processes can be clearly seen.
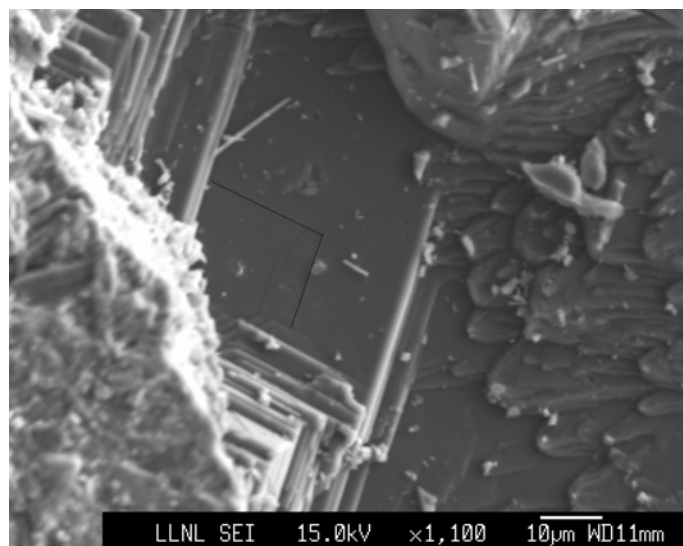

Figure 2. SEM photo showing etch pit on dissolving calcite at core entrance sample. The mineral crust is at the lower left.

In Figure 2 we have marked two sides of a large etch pit to illustrate that this sample from the entrance to the core is clearly undersaturated at this location underneath the overlying crust of secondary mineral grains. In Figure 3 it can be seen that, although the crust is quite thick, it is not a complete barrier to the bulk solution, hence calcite can remain undersaturated. EDS analyses of the crust show it to be strontianite.

Toward the exit of the core the calcite grains still show evidence of dissolution, although etch pits in AFM images (Fig. 4) also show evidence of either backfilling with calcite (or high-Sr calcite) or, more likely, dissolution under near equilibrium conditions. A few isolated grains of strontianite can also be found.

The XRD analyses done on each section of core show clearly that strontianite abundance is high (> 5%) over the first 10 cm, but then decreases further along the core. It is most abundant a few cm into the core (Fig. 5).
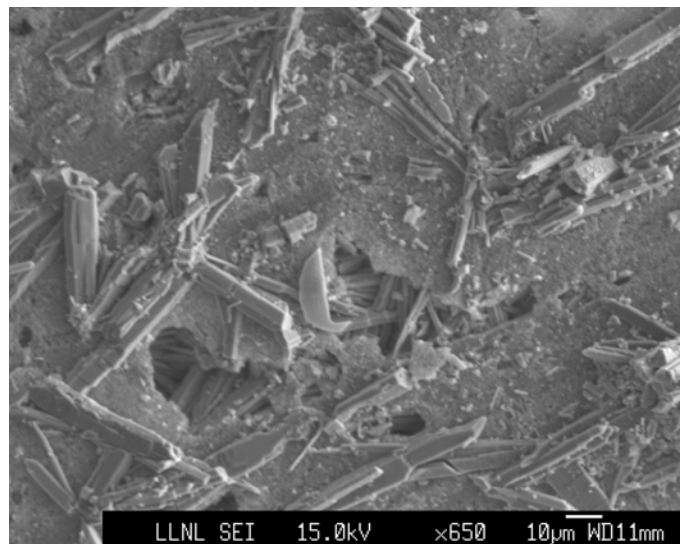

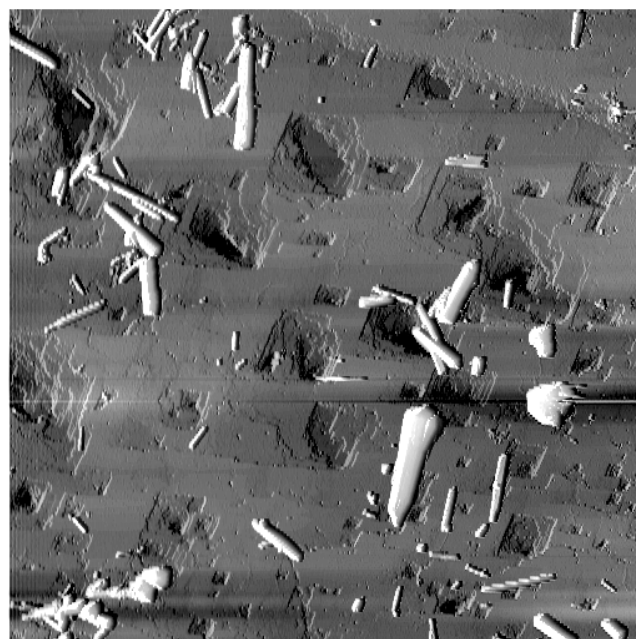Figure 3. SEM photo of strontianite crust at core entrance.

Figure 4. Blended height and deflection contact mode AFM images of core exit sample. Scan length is 20 μm.

5.2 CRUNCH reactive transport simulation

As seen in Figure 6, the reactive transport simulation predicts that steady-state is achieved quite quickly. This steady-state in the simulation results from rapid equilibration with calcite and rapid and abundant precipitation of strontianite.

Part of the lag in measured vs. predicted concentrations results from the time required for the furnace to heat up to run temperature. This offsets the measured values to longer time. Although the trends are in good agreement, the simulation over-predicts the Ca concentration slightly (and consequently under-predicts the pH), while it more significantly under-predicts the Sr concentration (probably from over-predicting the strontianite growth rate).
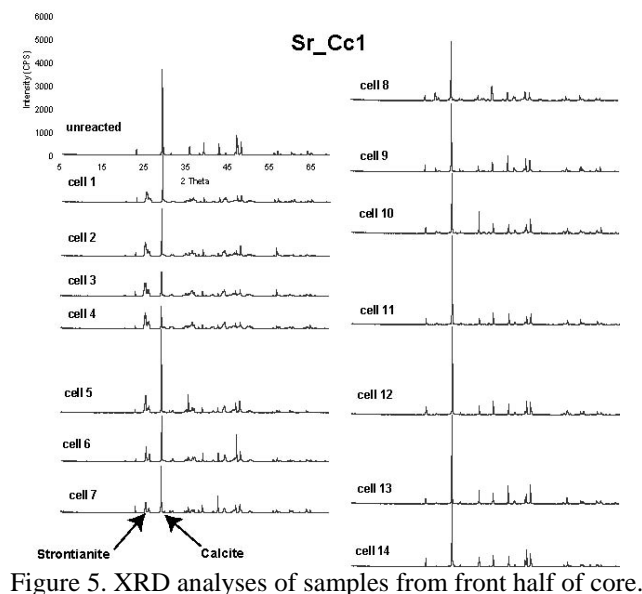
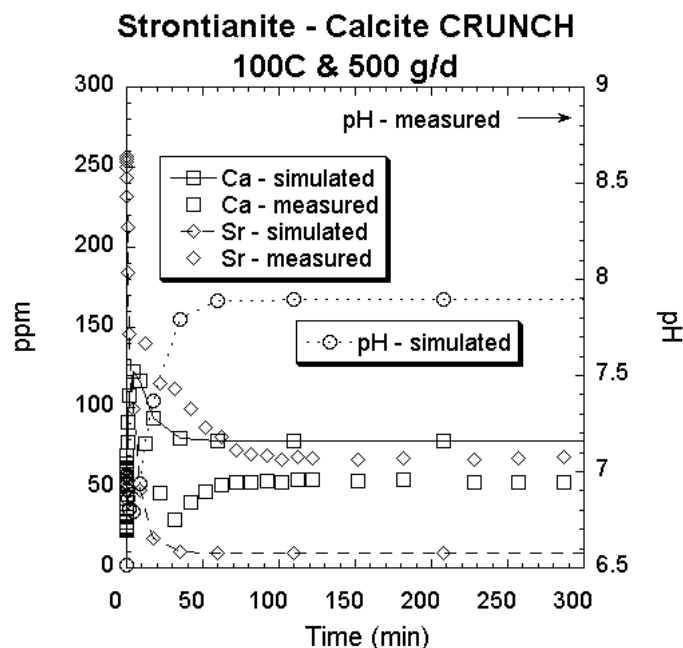Figure 5. XRD analyses of samples from front half of core.

Figure 6. Plot of simulator and PFR experiment results.

The simulation also predicts (Fig. 7) extensive calcite dissolution in the front of the core and abundant strontianite growth throughout much of the core, peaking at about 1 cm. Comparing the simulation to the XRD data (Fig. 5), the model has over-predicted both calcite dissolution and strontianite growth, especially at the front of the core.

Reconciling the physical and computational models can be accomplished in several ways. The physical model should include direct measurement of in situ carbonate concentration. This simply requires that samples be collected in gas-tight syringes pre-loaded with NaOH to prevent CO_2 evolution. We elected not to do this in the first experiment to gather more frequent cation samples. The 25°C measured pH will always be subject to error caused by partial equilibration with the atmosphere as it

cools, so the requirement to calculate in situ pH will remain. The model must be able to account for partially occluded surface area, when thick crusts form, and the present growth formalism (running the dissolution rate law backwards) clearly needs to be expanded to accommodate more realistic mineral growth rate laws.
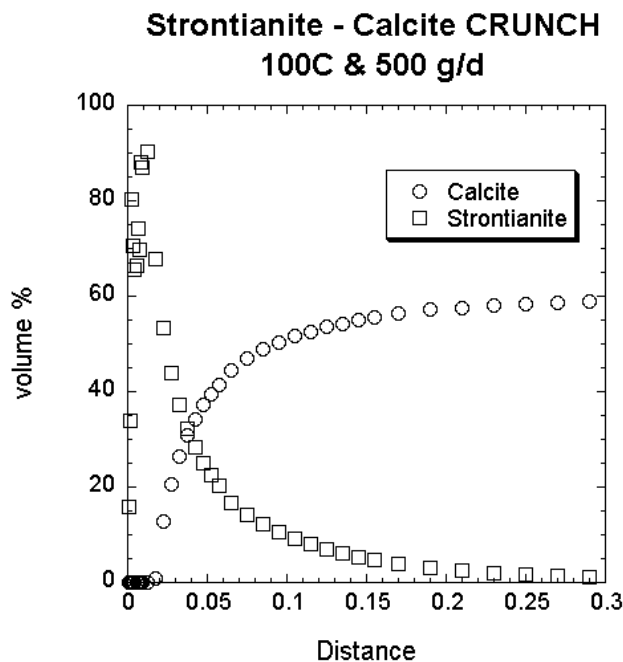

Figure 7 Plot of simulator predicted mineral distribution after 14 days.

6 CONCLUSION

Changes to rate law formalisms in our simulators can bring model predictions in line with macroscopic ideal physical model results. In this way we validate the reactive transport simulators, a critical step in their confident use.

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